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(54) CONVERSION OF 1,2,5,6-HEXANETETROL (HTO) TO TETRAHYDROFURAN DICARBOXYLIC ACID (THFDCA)

UMWANDLUNG VON 1,2,5,6-HEXANETETROL (HTO) IN TETRAHYDROFURAN-DICARBONSÄURE (THFDCA)

CONVERSION DE 1,2,5,6-HEXANETÉTROL (HTO) EN ACIDE DICARBOXYLIQUE DE TÉTRAHYDROFURANE (THFDCA)

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- **LE SEUR HENRY R. ET AL: "Formation of Heterocyclic Compounds. Part II. Action of Bases on the aa'-Dibromo-derivatives of Certain Dicarboxylic Acids", JOURNAL OF THE CHEMICAL SOCIETY, vol. 97, 1 January 1910 (1910-01-01), pages 173-185, XP055794551, ISSN: 0368-1769**
- **ASANO, T. et al.: "Selective hydrodeoxygenation of 2-furancarboxylic acid to valeric acid over molybdenum-oxide-modified platinum catalyst", ACS Sustainable Chemistry & Engineering, vol. 4, no. 12, 2016, pages 6253-6257, XP055645061,**

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Description

TECHNICAL FIELD

[0001] The present invention relates to conversion of 1,2,5,6-hexanetetrol (HTO) to tetrahydrofuran dicarboxylic acid (THFDCA).

BACKGROUND ART

[0002] Biomass contains carbohydrates or sugars that can be converted into value added products. Production of biomass-derived products for non-food uses is a growing industry. Bio-based fuels are an example of an application with growing interest. Another application of interest is the use of biomass as feedstock for synthesis of various industrial chemicals from renewable hydrocarbon sources.

[0003] In recent years, an increasing effort has been devoted to find ways to utilize biomass as feedstock for the production of organic chemicals because of its abundance, renewability, and worldwide distribution. When considering possible downstream chemical processing technologies, the conversion of sugars to value-added chemicals is very important.

[0004] Heterogeneous catalysts are widely used in liquid phase oxidation reactions. Oxidation of alcohols, aldehydes and carbohydrates has mainly focused on the use of supported Pd and Pt catalysts. The catalytic reactions occur under mild conditions in the range of about 20 to 80°C, and at atmospheric pressure. Dimitratos et al. reported the use of Pd and Pt catalysts for selective oxidation of alcohols to organic acids. Dimitratos et al, Pd and Pt catalysts modified by alloying with Au in the selective oxidation of alcohols, Catalysis Letters, vol. 244, pp. 115-121 (2006).

[0005] Other examples of use of Pd and Pt catalysts in liquid phase oxidation reactions are disclosed in Bronnimann et al. Direct oxidation of L -sorbose to 2-keto-L-gluconic acid with molecular oxygen on platinum -and palladium based catalysts, Catalysis, vol. 150, pp. 199-203 (1994); Garcia et al., Chemoselective catalytic oxidation of glycerol with air on platinum metals, Applied Catalysis A: General, vol. 127, pp. 165-176 (1995); and Hronec et al., Competitive oxidation of alcohols in aqueous phase using Pd/C catalyst, Molecular Catalysis, vol. 83, pp. 75-82 (1993).

[0006] Oxidation of cinnamyl alcohol to cinnamyl aldehyde over Pt and/or Pd catalysts has been reported. For example, Mallat et al., Catalyst potential: a key for controlling alcohol oxidation in multiphase reactors, Catalysis Today, vol. 24, pp. 143-150 (1995), reported the selective aerial oxidation of cinnamyl alcohol to cinnamaldehyde over Pt supported on alumina gave 88.5% selectivity to cinnamaldehyde.

[0007] Other examples of oxidation of cinnamyl alcohol to cinnamyl aldehyde over Pt and/or Pd catalysts are disclosed in Mallat et al., Selective oxidation of cinnamyl alcohol to cinnamaldehyde with air over Bi-Pt/Alumina catalysts," Catalysis, vol. 153, pp. 131-143 (1995); Grunwaldt et al., In situ EXAFS study of Pd/Al2O3 during aerobic oxidation of cinnamyl alcohol in an organic solvent, Catalysis, vol. 213, pp. 291-295 (2003); and Hardacre et al., Use of a rotating disc reactor to investigate the heterogeneously catalysed oxidation of cinnamyl alcohol in toluene and ionic liquids, Catalysis, vol. 232, pp. 355-365 (2005).

[0008] Direct oxidation of a primary alcohol without the presence of a functional group has not been widely studied under mild conditions with oxygen.

[0009] U.S. 9,593,064 discloses methods for synthesizing an ester or a carboxylic acid from an organic alcohol. The patent discloses that to form an ester, an alcohol is reacted with methanol or ethanol, in the presence of oxygen gas and a catalyst comprising palladium and a co-catalyst comprising bismuth, tellurium, lead, cerium, titanium, zinc and/or niobium (most preferably at least bismuth and tellurium). The patent discloses that, alternatively, that catalyst can be used to generate an acid from that alcohol, when water is also added to the reaction mix.

[0010] U.S. 9,409,506 discloses a method for preparing 2,5-furandicarboxylic acid (FDCA) by oxidizing 5-hydroxymethylfurfural (HMF) in water in the presence of a weak base and a supported catalyst comprising platinum and bismuth, in which the Bi/Pt molar ratio in the catalyst is between 0.1 and 0.3, and preferably between 0.15 and 0.3.

[0011] U.S. 8,501,989 discloses processes for producing an adipic acid product comprising the step of hydrodeoxygenating a tetrahydrofuranic substrate, e.g., tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) by reacting the same with hydrogen in the presence of a hydrodeoxygenation catalyst (i.e., catalyst suitable for the step of hydrodeoxygenation), an added source of halogen and a solvent, to convert at least a portion of the tetrahydrofuranic substrate to an adipic acid product. The patent discloses preparing THFDCA from FDCA, and that FDCA can be produced from 5-hydroxymethylfurfural (HMF) by selective oxidation. The patent further discloses that adipic acid can be converted to a wide variety of downstream chemical products or intermediates including adipate esters, polyesters, adiponitrile, hexamethylene diamine (HMDA), caprolactam, caprolactone, 1,6-hexanediol, aminocaproic acid, and polyamide such as nylons.

[0012] Yuan Qingqing et al.: "Bio-Based Chemicals: Selective Aerobic Oxidation of Tetrahydrofuran-2,5-dimethanol to Tetrahydrofuran-2,5-dicarboxylic Acid Using Hydrotalcite-Supported Gold Catalysts", ACS SUSTAINABLE CHEMISTRY & ENGINEERING, vol. 7, no. 5, 30 January 2019, pages 4647-4656 **discloses a route for the synthesis of**

THFDCA starting from 5-hydroxymethylfurfural (HMF) via oxidation of tetrahydrofuran dimethanol over hydrotalcite-supported gold nanoparticle catalysts in water.

[0013] Le Seur Henry R. et al.: "Formation of Heterocyclic Compounds. Part II. Action of Bases on the aa'-Dibromo-derivatives of Certain Dicarboxylic Acids", JOURNAL OF THE CHEMICAL SOCIETY, vol. 97, 1910, pages 173-185**, discloses the formation of THFDCA from 2,5-dihydroxyadipic acid in water at 200 °C for 3 h in a sealed tube.**

[0014] WO 2015/156803 A1 **discloses methods for synthesizing HTO, HDO and other reduced polyols from C5 and C6 sugar alcohols or R-glycosides.**

[0015] There remains a need in the art for alternative chemical synthesis strategies for producing useful intermediates and/or products, e.g., THFDCA (a diacid), 2,5-anhydro-3,4-dideoxy-hexanoic acid (the monoacid corresponding to THFDCA), and adipic acid, particularly strategies involving readily available or obtainable sugars and having the flexibility of synthesizing a number of different products with commercially attractive yields.

SUMMARY OF THE INVENTION

[0016] In each of its various embodiments, the present invention fulfills the need for more efficient production of useful intermediates and/or products from readily available or obtainable sugars. In an aspect, the present invention provides more efficient production of useful intermediates and/or products from 1,2,5,6-hexanetetrol (HTO), which itself can be derived from a sugar. In an aspect, a process is provided for production of THFDCA from 1,2,5,6-hexanetetrol (HTO). The process comprises the steps of (a) ring closing to form a ring compound and (b) oxidizing using a catalyst comprising platinum and bismuth to form an acid mixture. In an embodiment, the catalyst may comprise 5% Pt(Bi) by weight on carbon. Step (a) may be performed before or after step (b).

[0017] When step (a) is performed before step (b), then step (a) comprises contacting HTO with an acid for a time sufficient to form the ring compound, wherein the formed ring compound is tetrahydrofuran dimethanol (also known as 2,5 bis (dimethyl) tetrahydrofuran). In an embodiment, the acid may be selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid. Further, when step (a) is before step (b), then step (b) comprises oxidizing the tetrahydrofuran dimethanol formed in step (a) while the tetrahydrofuran dimethanol is in contact with the catalyst such that an acid mixture is formed comprising at least one of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) or 2,5-anhydro-3,4-dideoxy-hexanoic acid. **When** 2,5-anhydro-3,4-dideoxy-hexanoic acid is formed as part of the acid mixture, the process **further comprises** i) recovering the 2,5-anhydro-3,4-dideoxy-hexanoic acid from the acid mixture, ii) recovering the 2,5-anhydro-3,4-dideoxy-hexanoic acid from the acid mixture and oxidizing the same while in contact with a catalyst comprising platinum and bismuth to form THFDCA, or iii) oxidizing the 2,5-anhydro-3,4-dideoxy-hexanoic acid in the acid mixture while in contact with the catalyst used in step b) to form additional THFDCA.

[0018] When step (b) is performed before step (a), then step (b) comprises oxidizing HTO while the HTO is in contact with the catalyst such that an acid mixture comprising 2,5-dihydroxyadipic acid and 2-hydroxyglutaric acid is formed, wherein more 2,5-dihydroxyadipic acid is formed than 2-hydroxyglutaric acid. Further, when step (b) is performed before step (a), then step (a) comprises contacting 2,5-dihydroxyadipic acid formed in step (b) with an acid other than 2,5-dihydroxyadipic acid for a time sufficient to form the ring compound, wherein the formed ring compound is THFDCA. In an embodiment, the acid other than 2,5-dihydroxyadipic acid may be selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid.

[0019] In an aspect, a process as defined in claim 6 is provided for production of THFDCA and its corresponding monoacid, i.e., 2,5-anhydro-3,4-dideoxy-hexanoic acid. In this aspect, the process comprises oxidizing tetrahydrofuran dimethanol while the tetrahydrofuran dimethanol is in contact with a catalyst comprising Pt and Bi such that an acid mixture is formed comprising at least one of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) or its corresponding monoacid (2,5-anhydro-3,4-dideoxy-hexanoic acid).

[0020] In an aspect, a process is provided for production of THFDCA comprising oxidizing HTO while the HTO is in contact with a catalyst comprising Pt and Bi such that an acid mixture comprising 2,5-dihydroxyadipic acid and 2-hydroxyglutaric acid is formed, wherein more 2,5-dihydroxyadipic acid is formed than 2-hydroxyglutaric acid. **The** process comprises contacting the 2,5-dihydroxyadipic acid formed in the oxidizing step **with an acid other than 2,5-dihydroxyadipic acid for a time sufficient to form the ring compound, wherein the ring compound is THFDCA. In one embodiment, the acid other than 2,5-dihydroxyadipic acid is selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid.**

[0021] These and other aspects, embodiments, and associated advantages will become apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

FIG. 1 shows synthesis of THFDCA and its monoacid, 2,5-anhydro-3,4-dideoxy-hexanoic acid, from glucose according to certain aspects of the invention.

FIG. 2 shows synthesis of THFDCA from tetrahydrofuran dimethanol according to certain aspects of the invention.

[0023] The figures are to be understood to present embodiments of the invention to aid in understanding of the principles and reaction chemistry involved, but not to limit the scope of the invention as defined in the appended claims. As would be apparent to one of skill in the art having knowledge of the present disclosure, synthesis methods according to various other embodiments of the invention will utilize particular reagents and reaction conditions determined, at least in part, according to specific objectives.

DETAILED DESCRIPTION OF EMBODIMENTS

[0024] **The :** present invention discloses processes using a catalyst comprising Pt and Bi in an oxidizing step to form an acid mixture, wherein the acid mixture comprises THFDCA or an acid from which THFDCA may be synthesized.

[0025] In an aspect, a process is provided for production of THFDCA and its corresponding monoacid, i.e., 2,5-anhydro-3,4-dideoxy-hexanoic acid. In an aspect, the process comprises converting 1,2,5,6-hexanetetrol (HTO) to tetrahydrofuran dimethanol. **The** process comprises placing the tetrahydrofuran dimethanol in contact with a catalyst comprising Pt and Bi **and** oxidizing the tetrahydrofuran dimethanol while the tetrahydrofuran dimethanol is in contact with the catalyst such that an acid mixture is formed comprising at least one of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) or 2,5-anhydro-3,4-dideoxy-hexanoic acid. Monoacid (2,5-anhydro-3,4-dideoxy-hexanoic acid) in the acid mixture may be further oxidized using the Pt(Bi) catalyst to form the desired THFDCA product, optionally after being separated from any THFDCA originally formed in the acid mixture. In an embodiment, both acids are formed, wherein more THFDCA is selectively formed than its corresponding monoacid. In another embodiment, more 2,5-anhydro-3,4-dideoxy-hexanoic acid is formed than THFDCA.

[0026] In an aspect, a process is provided for production of THFDCA comprising oxidizing HTO while the HTO is in contact with a catalyst comprising Pt and Bi such that an acid intermediate mixture comprising 2,5-dihydroxyadipic acid and 2-hydroxyglutaric acid is formed, wherein more 2,5-dihydroxyadipic acid is formed than 2-hydroxyglutaric acid. **The process comprises contacting the 2,5-dihydroxyadipic acid formed in the oxidizing step with an acid other than 2,5-dihydroxyadipic acid for a time sufficient to form the ring compound, wherein the ring compound is THFDCA. In one embodiment, the acid other than 2,5-dihydroxyadipic acid is selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid.**

[0027] FIG. 1 illustrates two pathways for producing THFDCA from a sugar. The pathways are common to each other in the aspect that they each may comprise four stages of operation, with the first two stages of operation being the same for each pathway. The pathways are also common to each other in the aspect that they both involve ring closing to form a ring compound, and oxidation of a compound while the compound is in contact with a catalyst comprising Pt and Bi, at an elevated temperature. The pathways differ in that in one pathway, the ring closing occurs first, followed by the oxidation step, whereas in the second pathway, oxidation is conducted first, followed by ring closing. The pathways are identified as Pathway 1 and Pathway 2 in the description that follows.

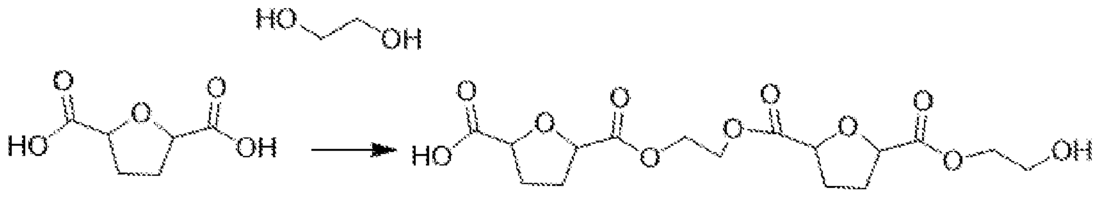
[0028] As shown in FIG. 1, in a first stage, a sugar, such as glucose, is hydrogenated so that it is converted to sorbitol. The first stage may be carried out under neutral conditions, at a relatively low temperature, at relatively low pressure, and in the presence of a hydrogenation catalyst. The hydrogenation catalyst may contain copper and/or ruthenium. When the hydrogenation catalyst comprises copper, the solution comprising glucose should contains less than 2 ppm sulfide anion and less than 1 ppm chloride anions. Exemplary ruthenium catalysts are selected from the group consisting of ruthenium supported on carbon, ruthenium supported on a zeolite, ruthenium supported on TiO_2, and ruthenium supported on Al_2O_3. With the benefit of this disclosure, those skilled in the art will recognize that this first stage may be conducted in accordance with hydrogenation techniques disclosed in US 2017/0029393, at temperatures of 150 degrees Celsius and greater, especially from 160 to 220 degrees Celsius, and hydrogen pressures of 4.1 MPa and greater (600 psi and greater), especially 4.1 MPa (600 psi) to 6.9 MPa (1000 psi), for from 2 to 4 hours in a reaction vessel.

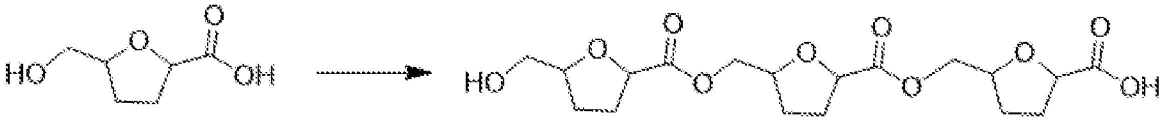
[0029] As shown in FIG. 1, in a second stage, sorbitol formed in the first stage may be converted to HTO. Those skilled in the art will recognize that, with the benefit of this disclosure, HTO may be produced from a C6 sugar alcohol, such as sorbitol (as shown in FIG. 1), and/or an R-glycoside in accordance with techniques disclosed in US 2017/0029393. For example, HTO may be synthesized from a starting compound that is C6 sugar alcohol and/or a C6 R-glycoside (wherein R is an alkyl moiety) present as at least 20% wt/wt in a solution comprising water by hydrogenation with hydrogen in the presence of a Raney copper catalyst, particularly by hydrogenation with the Raney copper catalyst deployed as a fixed bed in a reactor at temperatures of from 175 to 250 degrees Celsius and hydrogen pressures between 3.4 MPa to 17.2 MPa (500 to 2500 psi) at an average residence time of 2 hours in a continuous mode or between 1 and 4 hours in a batch mode. The sugar alcohols can be obtained from a commercial source or derived from any known method in the industry. In certain embodiments the sugar alcohols may be obtained by hydrogenation of C6 sugars or C6 R-glycosides. For example, sorbitol is typically obtained by hydrogenation of glucose over a Raney nickel catalyst. Ethyl glucoside may be obtained by hydrogenation of an acetyl cellulose pulp according to the methods described in US 2017/0029393. The R-glycoside can be obtained from a commercial source or derived from any known method in the industry. In certain embodiments the R-glycoside is an ethyl glucoside obtained from acylated cellulose pulp as described in US 2017/0029393. The reaction, however, can use any R-glycoside where the R group is a C1 to C4 alkyl group. Most preferably the R group is methyl or ethyl with the most commonly available glycosides being methyl glucoside or ethyl glucoside.

[0030] In Pathway 1, a third stage may be conducted under relatively mild conditions to convert HTO to a ring compound. In the third stage of Pathway 1, HTO may be contacted with an acid selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid (e.g., bismuth and scandium triflates or other triflates) for a time sufficient to form a ring compound, wherein the formed ring compound is tetrahydrofuran dimethanol (also known as 2,5 bis (dimethyl) tetrahydrofuran). With the benefit of this disclosure, those skilled in the art will recognize that this third stage of Pathway 1 may be conducted in accordance with HTO-to-2,5 bis (dimethyl) tetrahydrofuran (i.e., tetrahydrofuran dimethanol) conversion techniques disclosed in US 2017/0029393, using from 0.05% to 5% mol/mol of the starting materials of the acid catalyst, under reduced pressures ranging from 20 kPa (3.0 psi) to 40 kPa (6.0 psi) to facilitate continuous water removal and at temperatures from 120 to 150 degrees Celsius over from 1 to 4 hours.

[0031] In Pathway 1, the fourth stage **comprises** oxidation of tetrahydrofuran dimethanol to a form an acid mixture of at least one of THFDCA or 2,5-anhydro-3,4-dideoxy-hexanoic acid, in the presence of a catalyst comprising Pt and Bi, e.g., 5% Pt(Bi) by weight on carbon. As shown in FIG. 1, the fourth stage of Pathway 1 may be carried out at an elevated temperature, e.g., 150°C. When oxidation of tetrahydrofuran dimethanol is carried out at such an elevated temperature, both acids are formed, wherein more THFDCA is formed than its corresponding monoacid 2,5-anhydro-3,4-dideoxy-hexanoic acid.

[0032] An alternative embodiment of the fourth stage of Pathway 1 is shown in FIG. 2. In this alternative embodiment, oxidation of tetrahydrofuran dimethanol may be conducted at 60°C and at atmospheric pressure in the presence of a catalyst comprising Pt and Bi, e.g., 5% Pt(Bi) by weight on carbon, to form the monoacid (2,5-anhydro-3,4-dideoxy-hexanoic acid), with no measurable yield of THFDCA. The benefit of the oxidation of tetrahydrofuran dimethanol to the monoacid under mild conditions is that it allows for easy control of reaction conditions. Further, the monoacid has potential for use in applications that differ from those considered for THFDCA. For example, the monoacid may be polymerized under conditions to form a polymer that is different from the polymer formed by the polymerization of THFDCA. Further, polymerization of THFDCA typically requires reaction with a dialcohol. Compare the following polymerization reactions of THFDCA versus polymerization of the monoacid:





As shown in FIG. 2, when desired, of course, monoacid produced in the absence of measurable THFDCA may also be converted to the diacid THFDCA by oxidizing the monoacid at 150°C in the presence of a catalyst comprising Pt and Bi, e.g., 5% Pt(Bi) by weight on carbon to form THFDCA. The time period for oxidation of the monoacid to the diacid can be shortened by conducting the oxidation at an elevated pressure greater than atmospheric pressure, for example, about 6.9 MPa (1000 psi) air.

[0033] As shown in FIG. 1, in Pathway 2, the third stage **comprises oxidation of HTO to 2,5-**dihydroxyadipic acid. In the third stage of Pathway 2, HTO is oxidized at an elevated temperature, e.g., about 150°C, at atmospheric pressure, in the presence of a catalyst comprising Pt and Bi, e.g., 5% Pt(Bi) by weight on carbon, to form 2,5-dihydroxyadipic acid.

[0034] In Pathway 2, the fourth stage **comprises** contacting 2,5-dihydroxyadipic acid formed in stage 3 with an acid in an amount and manner for ring closing, thereby converting 2,5-dihydroxyadipic acid to THFDCA . This ring closing step may be performed by contacting 2,5-dihydroxyadipic acid with an acid selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid for a time sufficient to form THFDCA.

[0035] With the benefit of this disclosure, those skilled in the art will recognize that this fourth stage of Pathway 2 may be conducted in accordance with the same ring closing techniques disclosed in US 2017/0029393 and referenced above in connection with the third stage of Pathway 1.

[0036] The THFDCA formed in accordance with Pathway 1 or Pathway 2 may be separated from other compounds, e.g., the corresponding monoacid, i.e., 2,5-anhydro-3,4-dideoxyhexonic acid, that may be present. For example, this separation may be performed using ion-exclusion chromotography (IEC) and/or ion-exchange (IX), for example, by means of a polymethacrylate-based weakly acidic cation exchange resin using ion exclusion chromatography under acidic elution conditions, as described in Tanaka et al., "Separation of carboxylic acids on a weakly acidic cation-exchange resin by ion-exclusion chromatography", Journal of Chromatography A, vol. 850, no. 1, pp. 187-196 (Aug. 1999) or by means of an anion exchange medium as taught by US 9,487,465, "Process for the Separation of Mono- and Di-Carboxylic Acid Compounds".

[0037] With the benefit of this disclosure, those skilled in the art will recognize that THFDCA, produced using either Pathway 1 or Pathway 2, may be readily converted to adipic acid. For example, THFDCA may be converted to adipic acid by reacting the THFDCA with hydrogen, in the presence of a hydrodeoxygenation catalyst, a solvent and a source of halogen. The solvent may comprise a weak carboxylic acid. The term "weak carboxylic acid" as used herein means any unsubstituted or substituted carboxylic acid having a pKa of at least about 3.5, more preferably at least about 4.5 and, more particularly, is selected from among unsubstituted acids such as acetic acid, propionic acid or butyric acid, or mixtures thereof. Among the useful solvents, acetic acid is more preferred because it also is useful as a solvent in the subsequent hydrodeoxygenation of THFDCA. With the benefit of this disclosure, those skilled in the art will recognize that the conversion of THFDCA to adipic acid may be conducted in accordance with the THFDCA-to-adipic acid conversion techniques disclosed in U.S. 8,501,989, by reacting THFDCA with hydrogen in the presence of hydrogen iodide or hydrogen bromide and a solvent such as acetic acid, at temperatures from about 80 to about 200 degrees Celsius and especially from about 140 to about 180 degrees Celsius, with a partial pressure of hydrogen of from about 1379 kPa (200 psia) to about 13790 kPa (2000 psia), especially from about 2758 kPa (400 psia) to about 10343 kPa (1500 psia), in the presence of a solid phase hydrodeoxygenation catalyst comprising one or more d-block metals (Ru, Rh, Pd, Pt) which may be used alone, in combination with one or more rare earth metals (lanthanides) and with one or more main group metals (Al, Ga, Tl, In, Sn, Pb or Bi), on a support.

[0038] In an aspect, a process is provided comprising placing tetrahydrofuran dimethanol in contact with a catalyst comprising Pt and Bi. The process comprises oxidizing the tetrahydrofuran dimethanol while the tetrahydrofuran dimethanol is in contact with the catalyst such that an acid mixture comprising tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) and corresponding monoacid (2,5-anhydro-3,4-dideoxy-hexanoic acid) is formed, wherein more THFDCA is selectively formed than the corresponding monoacid. In an embodiment, the oxidizing step is conducted at a temperature of about 145°C to 155°C, and preferably about 148°C to 152°C, and more preferably about 150°C. In an embodiment, the oxidizing step is conducted at a pressure of about **6.9 MPa (1000 psi) air.**

[0039] In an aspect, a process is provided comprising placing tetrahydrofuran dimethanol in contact with a catalyst comprising Pt and Bi. The process comprises oxidizing the tetrahydrofuran dimethanol while the tetrahydrofuran dimethanol is in contact with the catalyst at a first temperature and first pressure such that an acid mixture is formed comprising at least one of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) or its corresponding monoacid (2,5-anhydro-3,4-dideoxy-hexanoic acid), wherein more corresponding monoacid is selectively formed than THFDCA. In an embodiment, the first temperature may be about 55°C to 65°C, and preferably about 58°C to 62°C, and more preferably about 60°C. In an embodiment, the first pressure is at atmospheric pressure.

[0040] In an aspect, the process may further comprise placing the monoacid 2,5-anhydro-3,4-dideoxy-hexanoic acid in contact with a catalyst comprising Pt and Bi, and oxidizing the monoacid while the monoacid is in contact with the catalyst at a second temperature and second pressure such that a majority of the monoacid is converted to THFDCA. In an embodiment, the second temperature may be about 145°C to 155°C, and preferably about 148°C to 152°C, and more preferably about 150°C. In an embodiment, the second pressure about **6.9 MPa (1000 psi) air.**

[0041] In an aspect, a process is provided for production of THFDCA comprising oxidizing HTO while the HTO is in contact with a catalyst comprising Pt and Bi such that an acid intermediate mixture comprising 2,5-dihydroxyadipic acid and 2-hydroxyglutaric acid is formed, wherein more 2,5-dihydroxyadipic acid is formed than 2-hydroxyglutaric acid. In an embodiment, this oxidizing step is conducted at atmospheric pressure and a temperature of 145°C to 155°C, and preferably about 148°C to 152°C, and more preferably about 150°C. In a further aspect, the process comprises contacting the 2,5-dihydroxyadipic acid formed in the oxidizing step with an acid selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid for a time sufficient to form the ring compound, wherein the formed ring compound is THFDCA.

[0042] In an aspect, the present invention discloses oxidizing a primary alcohol with oxygen under mild conditions without the presence of a function group. In an aspect, a process and reaction system is disclosed wherein a sugar, such as glucose or dextrose, is ultimately converted to THFDCA, and THFDCA is converted to adipic acid. The reactor system may comprise four stages of operation, and each stage may be carried out in a separate reactor.

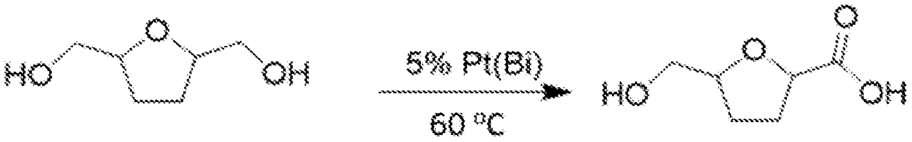
[0043] The following examples are set forth as representative of aspects of the present invention. These examples are not to be construed as limiting the scope of the invention as other equivalent embodiments will be apparent in view of the present disclosure and appended claims.

Examples

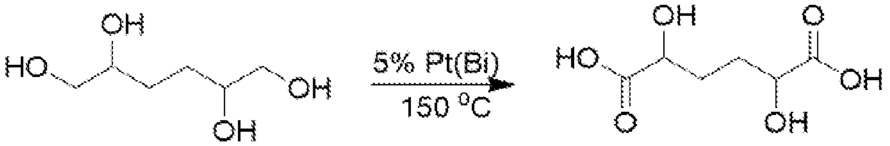
[0044] Example 1. Tetrahydrofuran dimethanol (35 g), 100 ml of de-ionized water and 2 g of the platinum-bismuth, were added to a 3-necked flask equipped with a condenser. The reaction mixture was refluxed and continuously stirred in an oil bath at 60°C. An aqueous solution of NaOH (21 g in 40 ml) was added drop wise, after finishing addition, the mixture was heated to 150°C for overnight (about 16 hours). During the course of the reaction, samples were withdrawn from the reaction mixture at regular time intervals and then stored at ambient condition before NMR analysis. Based on NMR data, the conversion of tetrahydrofuran dimethanol is 70% with 50% yield of THFDCA.

[0045] Example 2. Tetrahydrofuran dimethanol (4 g: cis/trans), 30 ml of de-ionized water, 2 g of NaOH and 0.5 g of the Pt(Bi)/C, were added to a 100 cc reactor. The reaction mixture was heated up to 150°C with 6.9 MPa (1000 psi) of air for 3 hours. Based on NMR data, the conversion of tetrahydrofuran dimethanol is above 98%, with 87% yield of THFDCA and 13% of the monoacid, 2,5-anhydro-3,4-dideoxyhexonic acid.

[0046] Example 3. Tetrahydrofuran dimethanol (35 g), 100 ml of de-ionized water and 2 g of the platinum-bismuth, were added to a 3-necked flask equipped with a condenser. The reaction mixture was refluxed and continuously stirred in an oil bath at 60°C. An aqueous solution of NaOH (21 g in 40 ml) was added drop wise, and after finishing addition, the mixture was heated to 60°C for overnight (about 16 hours). During the course of the reaction, samples were withdrawn from the reaction mixture at regular time intervals and then stored at ambient condition before NMR analysis. Based on NMR data, the conversion of tetrahydrofuran dimethanol is 91% with 89% yield of 2,5-Anhydro-3,4-dideoxyhexonic acid, and no measurable yield of THFDCA. The reaction is shown as follows (as well as in the upper portion of FIG. 2):



[0047] Example 4. 1,2,5,6-Hexanetetrol (HTO) 0.8 g, 0.8 g of the platinum-bismuth, and 1.0 g of NaOH in 20 ml of de-ionized water were added to a 3-necked flask equipped with a condenser. The reaction mixture was refluxed and continuously stirred in an oil bath at 60°C, the mixture was heated to 150°C for overnight (about 16 hours). During the course of the reaction, samples were withdrawn from the reaction mixture at regular time intervals and then stored at ambient condition before NMR analysis. Based on NMR data, the conversion of HTO is 78% with 2,5-dihydroxyadipic acid as majority product and 2-hydroxyglutaric acid as a minor product. This reaction is the third stage of Pathway 2, previously described above. This reaction is shown as follows (as well as in FIG. 1):



[0048] As can be seen from the above results, significant yields of THFDCA can be produced under the disclosed reaction conditions and with the described reaction mixture components. It is expected that process optimization, based on the teachings herein, can be conducted to increase yields of THFDCA, using HTO or tetrahydrofuran dimethanol according to the synthesis methods and overall teachings set forth in the present disclosure.

Claims

1. A process for synthesizing tetrahydrofuran-2,5-dicarboxylic acid (THFDCA), the process comprising:

(a) ring closing to form a ring compound; and
(b) oxidizing using a catalyst comprising platinum and bismuth to form an acid mixture;

wherein step (a) may be performed before or after step (b);
wherein when step (a) is performed before step (b), then step (a) comprises contacting 1,2,5,6-hexanetetrol (HTO) with an acid for a time sufficient to form the ring compound, wherein the formed ring compound is tetrahydrofuran dimethanol; and step (b) comprises oxidizing the tetrahydrofuran dimethanol formed in step (a) while the tetrahydrofuran dimethanol is in contact with the catalyst such that an acid mixture is formed comprising at least one of THFDCA or 2,5-anhydro-3,4-dideoxy-hexanoic acid, and when 2,5-anhydro-3,4-dideoxy-hexanoic acid is formed as part of the acid mixture, i) recovering the 2,5-anhydro-3,4-dideoxy-hexanoic acid from the acid mixture, ii) recovering the 2,5-anhydro-3,4-dideoxy-hexanoic acid from the acid mixture and oxidizing the same while in contact with a catalyst comprising platinum and bismuth to form THFDCA, or iii) oxidizing the 2,5-anhydro-3,4-dideoxy-hexanoic acid in the acid mixture while in contact with the catalyst used in step b) to form additional THFDCA;
wherein when step (b) is performed before step (a), then step (b) comprises oxidizing 1,2,5,6-hexanetetrol (HTO) while the HTO is in contact with the catalyst such that an acid mixture comprising 2,5-dihydroxyadipic acid and 2-hydroxyglutaric acid is formed, wherein more 2,5-dihydroxyadipic acid is formed than 2-hydroxyglutaric acid; and step (a) comprises contacting 2,5-dihydroxyadipic acid formed in step (b) with an acid other than 2,5-dihydroxyadipic acid for a time sufficient to form the ring compound, wherein the formed ring compound is THFDCA.

2. The process of claim 1, wherein

when step (a) is performed before step (b), then step (a) comprises contacting 1,2,5,6-hexanetetrol (HTO) with an acid selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid for a time sufficient to form the ring compound, wherein the formed ring compound is tetrahydrofuran dimethanol; and
wherein when step (b) is performed before step (a), then step (a) comprises contacting 2,5-dihydroxyadipic acid formed in step (b) with an acid other than 2,5-dihydroxyadipic acid for a time sufficient to form the ring compound, wherein the acid other than 2,5-dihydroxyadipic acid is selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid, wherein the formed ring compound is THFDCA.

3. The process of either of claim 1 or claim 2, wherein the 1,2,5,6-hexanetetrol (HTO) is derived from a C6 sugar alcohol or an R-glycoside, or a combination thereof.

4. The process of claim 3, wherein the C6 sugar alcohol is sorbitol.

5. The process of claim 4, wherein the sorbitol is derived from glucose.

6. A process comprising:

converting 1,2,5,6-hexanetetrol (HTO) to tetrahydrofuran dimethanol;
placing the tetrahydrofuran dimethanol in contact with a catalyst comprising Pt and Bi; and
oxidizing the tetrahydrofuran dimethanol while the tetrahydrofuran dimethanol is in contact with the catalyst such that an acid mixture is formed comprising at least one of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) or 2,5-anhydro-3,4-dideoxy-hexanoic acid.

7. The process of claim 6, wherein converting 1,2,5,6-hexanetetrol (HTO) to tetrahydrofuran dimethanol comprises contacting 1,2,5,6-hexanetetrol (HTO) with an acid for a time sufficient to form the ring compound, wherein the formed ring compound is tetrahydrofuran dimethanol.

8. The process of claim 7, wherein the acid is selected from the group consisting of sulfuric acid, phosphonic acid, carbonic acid and a water tolerant non-Bronsted Lewis acid.

9. The process of any of claims 6 through 8, wherein the catalyst comprises platinum and bismuth on a carbon support.

10. The process of any of claims 6 through 9, wherein both of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) and 2,5-anhydro-3,4-dideoxy-hexanoic acid are formed, and the THFDCA is separated from the 2,5-anhydro-3,4-dideoxy-hexanoic acid using ion-exclusion chromatography (IEC) or ion-exchange (IX), or a combination of thereof.

11. The process of claim 10, further comprising placing 2,5-anhydro-3,4-dideoxy-hexanoic acid in contact with the catalyst and oxidizing the 2,5-anhydro-3,4-dideoxy-hexanoic acid while in contact with the catalyst to produce additional THFDCA.

12. A process comprising:

(a) oxidizing 1,2,5,6-hexanetetrol (HTO) while the HTO is in contact with a catalyst comprising Pt and Bi such that an acid mixture comprising 2,5-dihydroxyadipic acid and 2-hydroxyglutaric acid is formed, wherein more 2,5-dihydroxyadipic acid is formed than 2-hydroxyglutaric acid; and
(b) contacting 2,5-dihydroxyadipic acid formed in step (a) with an acid other than 2,5-dihydroxyadipic acid for a time sufficient to form the ring compound, wherein the formed ring compound is THFDCA.

Patentansprüche

1. Verfahren zum Synthetisieren von Tetrahydrofuran-2,5-dicarbonsäure (THFDCA), wobei das Verfahren umfasst:

(a) Ringschluss unter Bildung einer Ringverbindung; und
(b) Oxidieren unter Verwendung eines Katalysators, der Platin und Bismut umfasst, unter Bildung eines Säuregemischs;

wobei Schritt (a) vor oder nach Schritt (b) durchgeführt werden kann;
wobei Schritt (a), wenn er vor Schritt (b) durchgeführt wird, das In-Kontakt-Bringen von 1,2,5,6-Hexantetrol (HTO) mit einer Säure während einer zur Bildung der Ringverbindung ausreichenden Zeit umfasst, wobei es sich bei der gebildeten Ringverbindung um Tetrahydrofurandimethanol handelt; und Schritt (b) das Oxidieren des in Schritt (a) gebildeten Tetrahydrofurandimethanols umfasst, während sich das Tetrahydrofurandimethanol in Kontakt mit dem Katalysator befindet, so dass ein Säuregemisch entsteht, das THFDCA und/oder 2,5-Anhydro-3,4-didesoxyhexansäure umfasst, und wenn 2,5-Anhydro-3,4-didesoxyhexansäure als Teil des Säuregemischs gebildet wird: i) Gewinnen der 2,5-Anhydro-3,4-didesoxyhexansäure aus dem Säuregemisch, ii) Gewinnen der 2,5-Anhydro-3,4-didesoxyhexansäure aus dem Säuregemisch und Oxidieren derselben, während sie mit einem Platin und Bismut umfassenden Katalysator in Kontakt ist, unter Bildung von THFDCA oder iii) Oxidieren der 2,5-Anhydro-3,4-didesoxyhexansäure in dem Säuregemisch, während sie mit dem in Schritt b) verwendeten Katalysator in Kontakt ist, unter Bildung von zusätzlichem THFDCA;
wobei Schritt (b), wenn er vor Schritt (a) durchgeführt wird, das Oxidieren von 1,2,5,6-Hexantetrol (HTO) umfasst, während sich das HTO mit dem Katalysator in Kontakt befindet, so dass ein Säuregemisch entsteht, das 2,5-Dihydroxyadipinsäure und 2-Hydroxyglutarsäure umfasst, wobei mehr 2,5-Dihydroxyadipinsäure als 2-Hydroxyglutarsäure entsteht; und Schritt (a) das In-Kontakt-Bringen von 2,5-Dihydroxyadipinsäure, die in Schritt (b) gebildet wurde, mit einer anderen Säure als 2,5-Dihydroxyadipinsäure während einer zur Bildung der Ringverbindung ausreichenden Zeit umfasst, wobei es sich bei der gebildeten Ringverbindung um THFDCA handelt.

2. Verfahren gemäß Anspruch 1, wobei Schritt (a), wenn er vor Schritt (b) durchgeführt wird, das In-Kontakt-Bringen von 1,2,5,6-Hexantetrol (HTO) mit einer Säure, die aus der Gruppe ausgewählt ist, die aus Schwefelsäure, Phosphonsäure, Kohlensäure und einer wassertoleranten Nicht-Brönsted-Lewis-Säure besteht, während einer zur Bildung der Ringverbindung aus-reichenden Zeit umfasst, wobei es sich bei der gebildeten Ringverbindung um Tetrahydrofurandimethanol handelt; und
wobei Schritt (a), wenn Schritt (b) vor Schritt (a) durchgeführt wird, das In-Kontakt-Bringen von 2,5-Dihydroxyadipinsäure, die in Schritt (b) gebildet wurde, mit einer anderen Säure als 2,5-Dihydroxyadipinsäure während einer zur Bildung der Ringverbindung ausreichenden Zeit umfasst, wobei die andere Säure als 2,5-Dihydroxyadipinsäure aus der Gruppe ausgewählt ist, die aus Schwefelsäure, Phosphonsäure, Kohlensäure und einer wassertoleranten Nicht-Brönsted-Lewis-Säure besteht, wobei es sich bei der gebildeten Ringverbindung um THFDCA handelt.

3. Verfahren gemäß Anspruch 1 oder 2, wobei das 1,2,5,6-Hexantetrol (HTO) von einem C6-Zuckeralkohol oder einem R-Glycosid oder einer Kombination davon abgeleitet ist.

4. Verfahren gemäß Anspruch 3, wobei es sich bei dem C6-Zuckeralkohol um Sorbit handelt.

5. Verfahren gemäß Anspruch 4, wobei der Sorbit von Glucose abgeleitet ist.

6. Verfahren, umfassend:

   Umsetzen von 1,2,5,6-Hexantetrol (HTO) zu Tetrahydrofurandimethanol;
   In-Kontakt-Bringen des Tetrahydrofurandimethanols mit einem Katalysator, der Pt und Bi umfasst; und
   Oxidieren des Tetrahydrofurandimethanols, während sich das Tetrahydrofurandimethanol in Kontakt mit dem Katalysator befindet, so dass ein Säuregemisch entsteht, das Tetrahydrofuran-2,5-dicarbonsäure (THFDCA) und/oder 2,5-Anhydro-3,4-didesoxyhexansäure umfasst.

7. Verfahren gemäß Anspruch 6, wobei das Umsetzen von 1,2,5,6-Hexantetrol (HTO) zu Tetrahydrofurandimethanol das In-Kontakt-Bringen von 1,2,5,6-Hexantetrol (HTO) mit einer Säure während einer zur Bildung der Ringverbindung ausreichenden Zeit umfasst, wobei es sich bei der gebildeten Ringverbindung um Tetrahydrofurandimethanol handelt.

8. Verfahren gemäß Anspruch 7, wobei die Säure aus der Gruppe ausgewählt ist, die aus Schwefelsäure, Phosphonsäure, Kohlensäure und einer wassertoleranten Nicht-Brönsted-Lewis-Säure besteht.

9. Verfahren gemäß einem der Ansprüche 6 bis 8, wobei der Katalysator Platin und Bismut auf einem Kohleträger umfasst.

10. Verfahren gemäß einem der Ansprüche 6 bis 9, wobei sowohl Tetrahydrofuran-2,5-dicarbonsäure (THFDCA) als auch 2,5-Anhydro-3,4-didesoxy-hexansäure entstehen und die THFDCA mit Hilfe von Ionenausschlusschromatographie (IEC) oder Ionenaustausch (IX) oder einer Kombination davon von der 2,5-Anhydro-3,4-didesoxyhexansäure getrennt wird.

11. Verfahren gemäß Anspruch 10, weiterhin umfassend In-Kontakt-Bringen von 2,5-Anhydro-3,4-didesoxyhexansäure mit dem Katalysator und Oxidieren der 2,5-Anhydro-3,4-didesoxyhexansäure, während sie sich mit dem Katalysator in Kontakt befindet, wobei zusätzliche THFDCA entsteht.

12. Verfahren, umfassend:

   (a) das Oxidieren von 1,2,5,6-Hexantetrol (HTO), während sich das HTO mit einem Katalysator, der Pt und Bi umfasst, in Kontakt befindet, so dass ein Säuregemisch entsteht, das 2,5-Dihydroxyadipinsäure und 2-Hydroxyglutarsäure umfasst, wobei mehr 2,5-Dihydroxyadipinsäure als 2-Hydroxyglutarsäure entsteht; und
   (b) In-Kontakt-Bringen von 2,5-Dihydroxyadipinsäure, die in Schritt (a) gebildet wurde, mit einer anderen Säure als 2,5-Dihydroxyadipinsäure während einer zur Bildung der Ringverbindung ausreichenden Zeit, wobei es sich bei der gebildeten Ringverbindung um THFDCA handelt.

Revendications

1. Procédé de synthèse de l'acide tétrahydrofuran-2,5-dicarboxylique (THFDCA), le procédé comprenant :

   (a) la cyclisation pour former un composé cyclique ; et
   (b) l'oxydation en utilisant un catalyseur comprenant du platine et du bismuth pour former un mélange acide ;

      dans lequel l'étape (a) peut être effectuée avant ou après l'étape (b) ;
      dans lequel lorsque l'étape (a) est effectuée avant l'étape (b), alors l'étape (a) comprend la mise en contact du 1,2,5,6-hexanetétrol (HTO) avec un acide pendant une durée suffisante pour former le composé cyclique, dans lequel le composé cyclique formé est le tétrahydrofurane diméthanol ; et l'étape (b) comprend l'oxydation du tétrahydrofurane diméthanol formé à l'étape (a) tandis que le tétrahydrofurane diméthanol est en contact avec le catalyseur de sorte qu'un mélange acide soit formé comprenant au moins l'un parmi THFDCA ou l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque, et lorsque l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque est formé en tant que partie du mélange acide, i) la récupération de l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque à partir du mélange acide, ii) la récupération de l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque à partir du mélange acide et son oxydation tout en étant en contact avec un catalyseur comprenant du platine et du bismuth pour former du THFDCA, ou iii) l'oxydation de l'acide 2,5-anhydro-3,4-didésoxy-

hexanoïque dans le mélange acide tout en étant en contact avec le catalyseur utilisé à l'étape b) pour former du THFDCA supplémentaire ;
dans lequel lorsque l'étape (b) est effectuée avant l'étape (a), alors l'étape (b) comprend l'oxydation du 1,2,5,6-hexanetétrol (HTO) tandis que le HTO est en contact avec le catalyseur de sorte qu'un mélange acide comprenant de l'acide 2,5-dihydroxyadipique et de l'acide 2-hydroxyglutarique soit formé, dans lequel une quantité d'acide 2,5-dihydroxyadipique supérieure à celle de l'acide 2-hydroxyglutarique est formée ; et l'étape (a) comprend la mise en contact de l'acide 2,5-dihydroxyadipique formé à l'étape (b) avec un acide autre que l'acide 2,5-dihydroxyadipique pendant une durée suffisante pour former le composé cyclique, dans lequel le composé cyclique formé est le THFDCA.

2. Procédé de la revendication 1, dans lequel

lorsque l'étape (a) est effectuée avant l'étape (b), alors l'étape (a) comprend la mise en contact du 1,2,5,6-hexanetétrol (HTO) avec un acide choisi dans le groupe constitué par l'acide sulfurique, l'acide phosphonique, l'acide carbonique et un acide de Lewis non-Bronsted tolérant l'eau pendant une durée suffisante pour former le composé cyclique, dans lequel le composé cyclique formé est le tétrahydrofurane diméthanol ; et
dans lequel lorsque l'étape (b) est effectuée avant l'étape (a), alors l'étape (a) comprend la mise en contact de l'acide 2,5-dihydroxyadipique formé à l'étape (b) avec un acide autre que l'acide 2,5-dihydroxyadipique pendant une durée suffisante pour former le composé cyclique, dans lequel l'acide autre que l'acide 2,5-dihydroxyadipique est choisi dans le groupe constitué par l'acide sulfurique, l'acide phosphonique, l'acide carbonique et un acide de Lewis non-Bronsted tolérant l'eau, dans lequel le composé cyclique formé est le THFDCA.

3. Procédé de la revendication 1 ou la revendication 2, dans lequel le 1,2,5,6-hexanetétrol (HTO) est dérivé d'un alcool de sucre en C6 ou d'un R-glycoside, ou d'une combinaison de ceux-ci.

4. Procédé de la revendication 3, dans lequel l'alcool de sucre en C6 est le sorbitol.

5. Procédé de la revendication 4, dans lequel le sorbitol est dérivé du glucose.

6. Procédé comprenant :

la conversion du 1,2,5,6-hexanetétrol (HTO) en tétrahydrofurane diméthanol ;
la mise en contact du tétrahydrofurane diméthanol avec un catalyseur comprenant du Pt et du Bi ; et
l'oxydation du tétrahydrofurane diméthanol tandis que le tétrahydrofurane diméthanol est en contact avec le catalyseur de sorte qu'un mélange acide soit formé comprenant au moins l'un parmi l'acide tétrahydrofuran-2,5-dicarboxylique (THFDCA) ou l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque.

7. Procédé de la revendication 6, dans lequel la conversion du 1,2,5,6-hexanetétrol (HTO) en tétrahydrofurane diméthanol comprend la mise en contact du 1,2,5,6-hexanetétrol (HTO) avec un acide pendant une durée suffisante pour former le composé cyclique, dans lequel le composé cyclique formé est le tétrahydrofurane diméthanol.

8. Procédé de la revendication 7, dans lequel l'acide est choisi dans le groupe constitué par l'acide sulfurique, l'acide phosphonique, l'acide carbonique et un acide de Lewis non-Bronsted tolérant l'eau.

9. Procédé de l'une des revendications 6 à 8, dans lequel le catalyseur comprend du platine et du bismuth sur un support en carbone.

10. Procédé de l'une des revendications 6 à 9, dans lequel l'acide tétrahydrofuran-2,5-dicarboxylique (THFDCA) et l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque sont tous deux formés, et le THFDCA est séparé de l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque en utilisant la chromatographie d'exclusion ionique (IEC) ou l'échange d'ions (IX), ou une combinaison de ceux-ci.

11. Procédé de la revendication 10, comprenant en outre la mise en contact de l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque avec le catalyseur et l'oxydation de l'acide 2,5-anhydro-3,4-didésoxy-hexanoïque tout en étant en contact avec le catalyseur pour produire du THFDCA supplémentaire.

12. Procédé comprenant :

(a) l’oxydation du 1,2,5,6-hexanetétrol (HTO) tandis que le HTO est en contact avec un catalyseur comprenant du Pt et du Bi de sorte qu’un mélange acide comprenant de l’acide 2,5-dihydroxyadipique et de l’acide 2-hydroxyglutarique soit formé, dans lequel une quantité d’acide 2,5-dihydroxyadipique supérieure à celle de l’acide 2-hydroxyglutarique est formée ; et

(b) la mise en contact de l’acide 2,5-dihydroxyadipique formé à l’étape (a) avec un acide autre que l’acide 2,5-dihydroxyadipique pendant une durée suffisante pour former le composé cyclique, où le composé cyclique formé est le THFDCA.

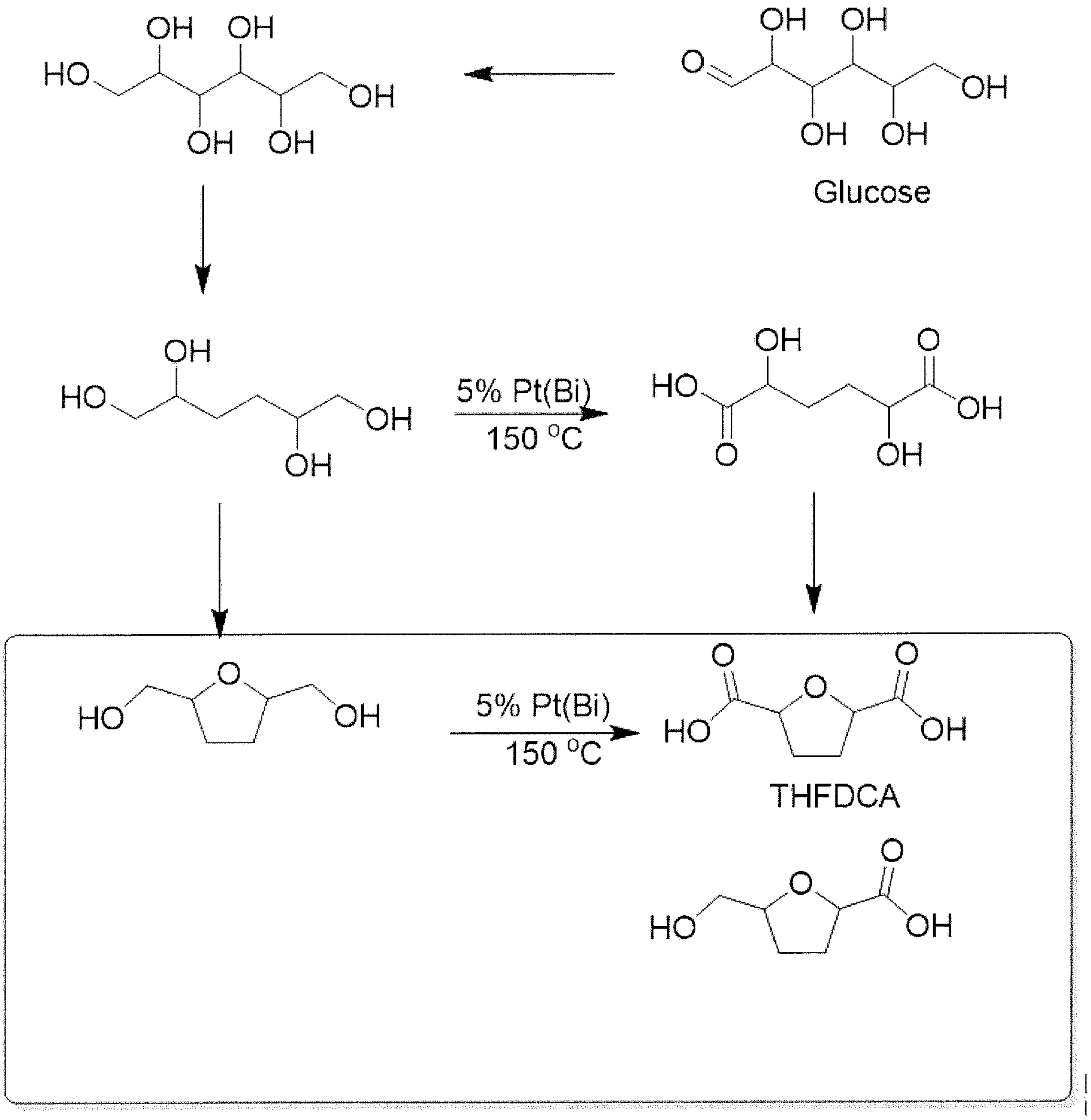


FIG. 1

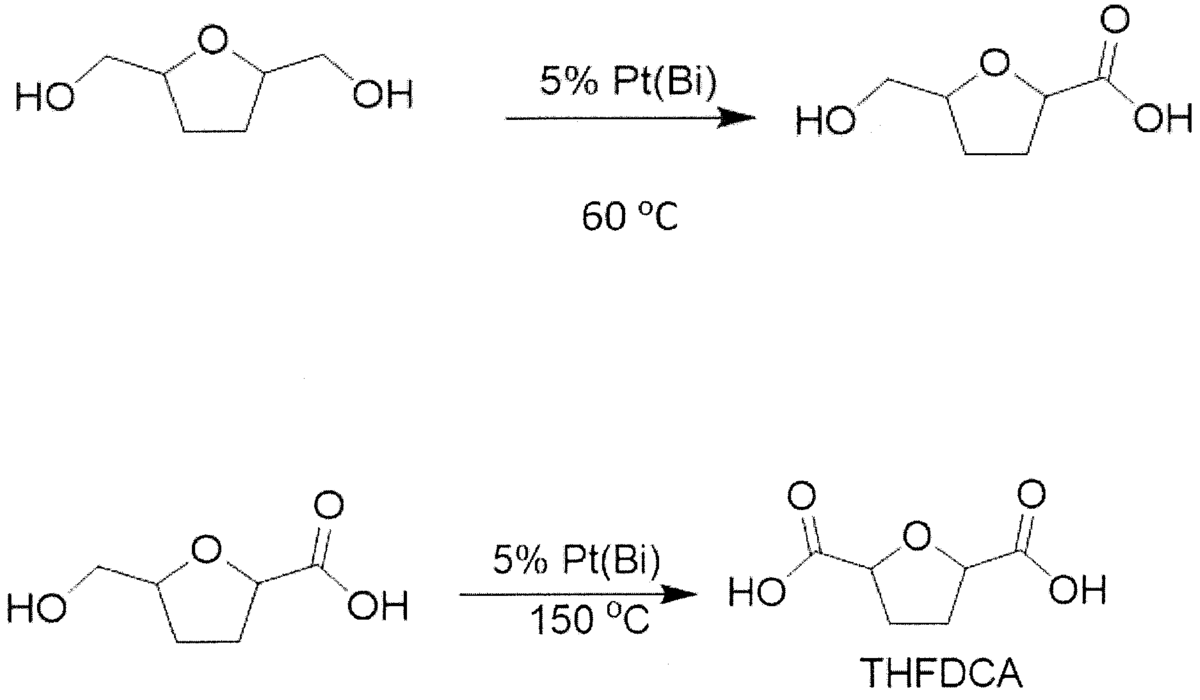


FIG. 2

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